Indian J. Phys. **52B**, 340-343 (1978)

Dense gas formulation of molten alkali halides II : critical constants

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(*Received* 16 *August* 1977, *revised* 14 *March* 1978)

The critical constants have been calculated for molten halides, using the dense gas formulation and compared with the experimental data and with the values given by Young & Alder (1971). The calculated results are found to be in better agreement with the experimental data.

1. Introduction

The critical constants, out of all the properties of the system, appear to be more sensitive so as to test the validity of any model or theory. Motivated by the work of Tosi & Fumi (1964), Young & Alder (1971), Woodcock & Singer (1971), Hansen & McDonald (1974, 1975) and Jacucci *et al* (1976), a calculation of critical constants for molten halides is presented in this communication. A model, based on dense gas formulation, similar to that given by Hansen & McDonald has already been utilized by the authors (Sharma & Sharma 1975 referred to as I hereafter) to calculate equilibrium properties of molten halides. In this model the diatomic molecule has been chosen as the basic unit which is treated as a hard sphere neutral pseudomolecule.

2. Calculation and Results

In accordance with these concepts, as in I we can write the pressure of the system as

$$\frac{PV}{Nk_BT} = \frac{P_hV}{Nk_BT} - A\left(\frac{V_m}{V}\right)^{1/3}\frac{k_BT_m}{k_BT}. \qquad \ldots (1)$$

Here k_B is the Boltzmann constant and T is the temperature (°K). N is the number of molecules in the system and V is the molar volume of the system. A is a dimensionless constant and the subscript m corresponds to the melting point. P is the total pressure, P_h corresponds to the pressure of a hard sphere system which is given by the equation of state (Carnahan & Starling 1969).

$$\frac{P_hV}{Nk_BT} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} \qquad \ldots (2)$$

where η is the packing fraction which is related with the hard sphere diameter σ by $\eta = \pi N\sigma^3/6V$. We determine A by assuming that the pressure of our system is zero, a reasonable physical criterion at the melting point. We further assume for molten halides, as in I, that at the melting point the packing fraction is nearly equal to 0·45, which yields

$$A = \frac{1+\eta_m+\eta_m^2-\eta_m^3}{(1-\eta_m)^3} = 9{\cdot}4. \qquad \ldots (3)$$

The calculation of the critical constants V_c, ρ_c (critical mass density), T_c and P_c is straightforward by differentiating eq. (1)

$$\frac{\partial P}{\partial V} = \frac{\partial^2 P}{\partial V^2} = 0.$$

These two equations along with eq. (1) are solved to yield

$$\eta_c = 0{\cdot}042479$$

which gives

$$V_c = 7{\cdot}427\times10^{24}\sigma^3, \qquad \rho_c = MN/V_c$$

$$T_c = 8{\cdot}94T_m(V_m/V_c)^{1/3} \quad \text{and} \quad P_c = \frac{RT_c}{V_c}\left[1{\cdot}19-9{\cdot}4\,\frac{T_m}{T_c}\left(\frac{V_m}{V_c}\right)^{1/3}\right], \quad \ldots (4)$$

where M is the pseudomolecular mass.

The calculated values of the V_c, ρ_c, T_c and P_c for NaCl and KCl are computed in table 1 and compared with the available experimental data (Janz 1967) as well as with the van der Waals model calculations (Young & Alder 1971). In table 2 we compare the calculated values of T_c for other alkali halides with the experimental data, which are found to lie close to the experimental data within about 22%.

3. Discussion of Results

It is satisfying to note from the tables that the present calculation is much better than that given by Young & Alder (1971) and in reasonable agreement with the experimental data. However, the compressibility factor $Z_c = P_cV_c/RT_c$ calculated here is around 0·15 which is close to one of the two experimental values quoted in the literature i.e., about 0·34 and 0·23. Further, with the availability of more information about the interatomic potentials which have recently been tested (Woodcock & Singer 1971, Hansen & McDonald 1974, 1975, Jacucci *et al* 1976), the computer experiments should be able to provide better understanding of critical constants.

Table 1. Comparison of the calculated values of the critical constants of alkali halides with the results of Young & Alder (1971) and with experimental data. The quantity inside the bracket represents the ratio of the calculated and average experimental values.

Critical constants	Present calculation (Ratio with exp.)	Young and Alder (Ratio with exp.)		Experiment	
		Ionic	Diatomic	A	B
		NaCl			
V_c (c.c.)	397·8(1·42)	129·6(0·46)	129·6(0·46)	266±60	293
ρ_c (gm/c.c.)	0·15(0·71)	0·45(2·14)	0·45(2·14)	0·22±0·05	0·20
T_c (°K)	4364(1·24)	6808(1·95)	4050(1·16)	3400±200	3600
P_c (bar)	128·9(0·44)	3139(10·72)	933(3·19)	350±125	235·5
		KCl			
V_c (c.c.)	517·2(1·15)	168·7(0·38)	168·7(0·38)	466±150	431
ρ_c (gm/c.c.)	0·145(0·82)	0·442(2·50)	0·442(2·50)	0·18±0·05	0·173
T_c (°K)	4244(1·35)	6717(2·14)	4870(1·55)	3200±200	3092
P_c (bar)	96·5(0·54)	2378(13·38)	862(4·85)	220±85	135·5

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Table 2. Comparison of the calculated and experimental values of critical temperatures (°K) of alkali halides. The experimental data are taken from Molten Salts Handbook (Janz 1967). The quantity in the bracket denotes the deviation (%) from the experiment.

Salt	T_c (°K)	
	Present calculation (difference %)	Experiment
LiF	4865 (+17·7)	4140
LiCl	3574 (+16·0)	3080
LiBr	3349 (+10·9)	3020
LiI	3042 (− 6·4)	3250
NaF	5160 (+20·8)	4270
NaBr	4150 (+29·7)	3200
NaI	3796 (+20·1)	3160
KF	4603 (+33·0)	3460
KBr	4097 (+29·2)	3170
KI	3882 (+30·2)	2980
RbF	4264 (+30·0)	3280
RbCl	4049 (+28·9)	3140
RbBr	3926 (+25·4)	3130
RbI	3746 (+23·4)	3035
CsF	3971 (+36·2)	2915
CsCl	3735 (+22·2)	3040
CsBr	3698 (+21·1)	3045
CsI	3658 (+21·1)	3020

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